Tuning Inner-Sphere Electron Transfer in a Series of Copper/Nitrosoarene Adducts
Mohammad Askari, Farshid Effaty, Federica Gennarini, Maylis Orio, Nicolas Le Poul, Xavier Ottenwaelder

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**INTRODUCTION**

The interaction of nitrosoarenes (ArNO) with metal centers has drawn much attention because of its relevance to biological pathways and catalytic C–N bond formation processes. Chemists now have a good understanding of the geometric structure of transition metal/nitrosoarene complexes. In addition, ArNO species are redox-noninnocent ligands, which portends a large landscape of electronic structures and reactivity types upon interaction with redox-active metal ions. Because ArNO species are isovalent with O₂, the reduction of ArNO by a transition metal is akin to the reduction of O₂ to the superoxide ion (O₂**, 1e reduction) or the peroxide ion (O₂**, 2e reduction). Therefore, metal/ArNO adducts are often regarded as surrogates for metal/O₂ adducts. In particular, and with relevance to the present paper, the activation of O₂ by Cu(I) centers is paramount in the biological world. This process fuels enzymes such as dopamine-β-hydroxylase, tyrosinase, and particulate methane monooxygenase, to name but a few. This has inspired numerous biomimetic studies in which an electron-rich Cu(I) species is reacted with O₂. Without protection of the protein backbone, however, the ensuing Cu/O₂ complexes are usually too oxidative to be stable above −60 °C. By contrast, Cu/ArNO adducts have been shown to have geometric and electronic structures very similar to those in Cu/O₂ adducts but were advantageously characterized at ambient temperature.

Owing to the asymmetric structure of ArNO in comparison with that of O₂, the structural variety of metal/nitrosoarene complexes exceeds that of metal/O₂ compounds. Some of the main bonding modes of ArNO to metal ions are shown in Scheme 1, with the most common one being through the N atom (κN). The other bonding modes are thought to be more prevalent when the ArNO moiety is reduced to the mono- or dianion.

The NO bond length in metal/ArNO complexes depends on the bonding mode, nature, and oxidation state of the metal and its supporting ligand. In this work we aimed to establish the nature of the charge-transfer transitions responsible for the intense green color of the complexes. In fine, this family of complexes is unique in that it walks through three redox states of the ArNO moiety while keeping the metal and its supporting ligand the same. This work provides snapshots of the reactivity of the toxic nitrosoarene molecules with the biologically relevant Cu(I) ion.

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**ABSTRACT:** A series of copper/nitrosoarene complexes were created that mimic several steps in biomimetic O₂ activation by copper(II). The reaction of the copper(I) complex of N,N,N′,N″-tetramethypropylenediamine with a series of para-substituted nitrobenzene derivatives leads to adducts in which the nitrosoarene (ArNO) is reduced by zero, one, or two electrons, akin to the isovalent species dioxygen, superoxide, and peroxide, respectively. The geometric and electronic structures of these adducts were characterized by means of X-ray diffraction, vibrational analysis, ultraviolet–visible spectroscopy, NMR, electrochemistry, and density functional theory (DFT) calculations. The bonding mode of the NO moiety depends on the oxidation state of the ArNO moiety: κN for ArNO, mononuclear μ-η¹-NO and dinuclear μ-η¹-μ-η² for ArNO**, and dinuclear μ-η¹-μ-η² for ArNO**. Isotopic labeling confirms the reduction state by measuring the NO stretching frequency (1392 cm⁻¹ for κN-ArNO, 1226 cm⁻¹ for μ-η¹-NO-ArNO**, 1133 cm⁻¹ for dinuclear μ-η¹-μ-η²-ArNO**, and 875 cm⁻¹ for dinuclear μ-η¹-μ-η² for ArNO**). The 15N NMR signal disappears for the ArNO** species, establishing a unique diagnostic for the radical state. Electrochemical studies indicate reduction waves that are consistent with one-electron reduction of the adducts and are compared with studies performed on Cu-O₂ analogues.

DFT calculations were undertaken to confirm our experimental findings, notably to establish the nature of the charge-transfer transitions responsible for the intense green color of the complexes. In fine, this family of complexes is unique in that it walks through three redox states of the ArNO moiety while keeping the metal and its supporting ligand the same. This work provides snapshots of the reactivity of the toxic nitrosoarene molecules with the biologically relevant Cu(I) ion.

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**Tuning Inner-Sphere Electron Transfer in a Series of Copper/ Nitrosoarene Adducts**

Mohammad S. Askari, Farshid Effaty, Federica Gennarini, Maylis Orio, Nicolas Le Poul,* and X. Ottenwaelder*

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the degree of reduction of the ArNO moiety, as was already shown with metal/O₂ adducts. A few studies have scrutinized the electronic structure on metal/ArNO complexes, particularly the oxidation state of the ArNO moiety, by means of techniques such as X-ray absorption spectroscopy or vibrational analysis with isotopic labeling (Scheme 2 for group 10 and 11 complexes). Their main conclusions are the following:

(i) In the majority of mononuclear κN nitrosarene complexes, the NO bond length, 1.209 – 1.31 Å, shows little or no elongation compared with that in free nitrosoarenes, unless back-bonding from the metal becomes significant. A radical character of the κN-ArNO moiety, and thus formally a 1.5 bond order, has been confirmed or inferred in a few species (Scheme 2a).

(ii) Most mononuclear κO complexes with non-d10 transition metals are structurally disordered, and conclusive statements about the extent of back-donation and ArNO reduction cannot be made. By contrast, the non-disordered crystal structures of [(Me₆tren)Cu(κO-PhNO)]X (X = TfO⁻, SbF₆⁻; Scheme 2b) show significant NO bond elongation. The radical character of the PhNO moiety (to an arylnitrosyl radical anion) was confirmed by magnetic measurements and vibrational and computational studies.

(iii) Dinuclear μ-η²:η¹ (end-on) complexes present varying degrees of ArNO reduction: by 0e (NO = 1.257 – 1.32 Å), 1e (1.33 – 1.35 Å), and 2e (1.37 – 1.49 Å; Scheme 2c).

(iv) In κ²-NO complexes, the NO bond length (1.323 – 1.432 Å) is significantly longer than that in free nitrosoarenes. Reduction of the ArNO moiety has been confirmed in Cu and Ni complexes (Scheme 2d). Further reduction of the Ni complex led to a doubly reduced PhNO²⁻ moiety. 2e reduction of the ArNO moiety was also confirmed in a square-planar Pd(II) species upon reaction of a Pd⁰ species with TolNO.

(v) Alongside several ArNO²⁻ examples (N–O = 1.40 – 1.53 Å), dinuclear μ-η²:η¹ complexes have been found in the solid-state structures of Cu complexes with shorter NO bond lengths (1.322 – 1.375 Å). Typically, the 1e-reduced ArNO⁺ moiety binds η¹ to a Cu(II) center and η² to a Cu(I) center (Scheme 2e). These species are thought to be in equilibrium with the mononuclear form [Cu²⁺(η²-ArNO⁺)] in solution.

(vi) Dinuclear μ-η²:η² complexes are quite rare, and only a few examples with Rh, Zr, Hf, Ni, and Cu are reported in the literature. With an NO bond length in the range of single bonds (1.422 – 1.500 Å), these complexes possess a doubly reduced ArNO⁻⁺ moiety. In the case of the Cu complex (Scheme 2f), this 2e reduction was made possible by using a very electron-poor nitrosoarene bearing a p-NO₂ substituent. More on this complex will be discussed below.

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### Scheme 1. Some Bonding Modes in Metal/Nitrosoarene Complexes, with Typical NO Bond Lengths

<table>
<thead>
<tr>
<th>Mode</th>
<th>NO Bond Length</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>κN</td>
<td>1.209 – 1.31 Å</td>
<td></td>
</tr>
<tr>
<td>κO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ-η²:η¹</td>
<td>1.374(4) Å</td>
<td>v(NO) = 1017 cm⁻¹</td>
</tr>
<tr>
<td>μ-η²:η²</td>
<td>1.374(4) Å</td>
<td>v(NO) = 1017 cm⁻¹</td>
</tr>
</tbody>
</table>

**Guide:**

- **Oxidation states:**
  - MII: MII
  - ArNO reduced by:
    - 1e: 2e

- **ArNO bond lengths:**
  - 2.5(2) Å
  - 2.5(2) Å
  - 3.5(2) Å
  - 2.6(2) Å

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### Scheme 2. Confirmed Examples of Group 10 and 11 Complexes in Which ArNO Gets Reduced by 1e or 2e upon Reaction

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“Asterisks indicate calculated values.”
To summarize, 1e reduction of the ArNO moiety is usually indicated by NO bond lengths in the range 1.29–1.37 Å and NO stretching frequencies in the range 1000–1300 cm⁻¹ (Scheme 2). Reduction by 2e is revealed by NO bond lengths of 1.36–1.46 Å and NO stretching frequencies below 950 cm⁻¹. When no reduction occurs, the NO bonds are short [1.261(4) and 1.268(4) Å for free PhNO], although these values can be modified significantly when back-bonding is present. Last, 4e reduction of PhNO, with complete NO bond cleavage, is possible with very electron-rich metal complexes such as cobalt(1) β-diketiminate species.

Noting that these examples comprise different supporting ligands and metal ions, we aimed at providing a systematic study of the degree of inner-sphere ArNO reduction by using a single Cu(I) precursor. Thus, in the present study, we report on adducts 3R (R = NMe₂, H, Cl, Br, NO₂) formed upon intermolecular reaction of para-substituted nitrosobenzenes 2R with the Cu(I) complex of N,N,N′,N′-tetramethyl-1,3-propanediamine (TMPD), 1 (Scheme 3), for which analogous Cu/O₂ chemistry is known.

**RESULTS AND DISCUSSION**

**Synthesis and Crystallography.** The slow addition of a [MeCN]₄Cu(TfO) (MeCN = acetonitrile) solution to a solution of TMPD and nitrosoarene, in a 1:1:1 ratio in tetrahydrofuran (THF) at 25 °C (1:1:2 for R = NO₂), results in the formation of deeply colored complexes that remain stable under inert conditions. Crystallization of the complexes by the slow diffusion of pentane into the reaction mixtures at −30 °C afforded crystals suitable for X-ray diffraction analysis. Several binding motifs consisting of mono- and dinuclear complexes are obtained depending on the para substituent of the nitrosoarene (Figure 1 and Table S1).

The structure of 3NMe₂ is that of a copper(I) arylnitroso complex, i.e., mere κN coordination of 1NMe₂ onto the [TMPD-Cu]⁺ complex. The N−O bond lengths in the two independent molecules, 1.281 and 1.293 Å, are consistent with a 1.5 bond order. The trigonal-planar ligand field of Cu is consistent with a Cu(I) oxidation state. In the solid state, the species dimerizes via two weak Cu···O interactions (2.242 and 2.278 Å) between two crystallographically related 3NMe₂ cations. This fact, coupled with the back-bonding of Cu into the nitroso π* orbital, could explain the slight elongation of the N−O bond compared with a true double bond.

Two types of crystals were obtained in the same crystallization pot with R = H. The minor component, of green color, is the mononuclear [TMPD-Cu II(η²-PhNO•−)(TfO)] (3H). This complex displays an η²-NO coordination with an elongated N−O bond of 1.327 Å, consistent with a 1.5 bond order. Cu sits in a square-pyramidal environment with a TfO⁻ anion as a weak axial ligand (Cu···O = 2.345 Å). The brown major component, 3H', of the formula [TMPD-Cu II(μ-η²:η¹-PhNO•)(μ-TfO)] also displays an elongated N−O bond of 1.345 Å, consistent with a 1.5 bond order. One of the Cu centers is bonded to both N and O of the PhNO moiety (Cu−N = 2.019 Å; Cu−O = 1.853 Å), while the other is only bonded to the N atom of PhNO (Cu−N = 1.904 Å; Cu−O = 1.701 Å).
2.828 Å. Species 3 explosives is therefore well described as formed from the association of the minor green component 3 with one molecule of 1 (Scheme 4). Such architecture and

Scheme 4. Mononuclear/Dinuclear Equilibrium in 3H Species

(major species in solution) (major species in the solid state)

“TiO” anions are not shown.

 association were already described in the literature.23,37

Because the mononuclear complex prevails in solution (the solution is green, and a Job titration confirms a 1:1 stoichiometry; Figure S14), formation of the dinuclear compound is an artifact of crystallization.

For 3O, only green crystals of [TMPDCuII(η2-2NO2)(TiO)] were formed. The molecular structure is very similar to that of 3H, with a 1.5 N–O bond order (1.3315 Å), except that the TiO– anion and the aromatic ring are on the same side of the CuNO plane.

The complex with the most electron-poor ArNO moiety, 3NO3, was characterized in a previous communication.25 It is a dinuclear species of the formula [TMPDCuII(μ-η2:η2-PhNO2-)(μ-TiO)CuII(TMPD)][TiO], where 2NO2 is reduced by 2e (N–O = 1.456 Å) and both Cu centers are in the 2+ oxidation state.

Overall, the crystallographic study concludes on an increased degree of electron transfer from 1 to 2H inasmuch as the p-R substituent is made more electron-poor: 0e in 3NMe3, 1e in 3H/1H, and 2e in 3NO3. The lability of Cu complements the self-assembly process by allowing TiO or extra Cu(I) coordination when necessary.

IR Properties. Vibrational analysis by IR spectroscopy was conducted on 2R precursors and 3R complexes, where the N atom of the nitroso moiety is either 14N or 15N. Synthesis of the 15N-labeled 2R precursors is provided in the Supporting Information. Isotopic labeling enables one to isolate the vibrations near the nitroso moiety from the rest of the molecule. In parallel, density functional theory (DFT) calculations were conducted to identify the nature of the modes observed (especially NO vs CN stretches in the ArNO moiety). Full data are given in the Supporting Information.

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Table 1. NO Stretching Frequencies

<table>
<thead>
<tr>
<th>species</th>
<th>ν (Δ)/cm⁻¹</th>
<th>species</th>
<th>ν (Δ)/cm⁻¹</th>
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</thead>
<tbody>
<tr>
<td>2NMe3</td>
<td>1365 (12), 1340 (19)</td>
<td>3NMe3</td>
<td>1392 (14), 1315 (6)</td>
</tr>
<tr>
<td>2H</td>
<td>1388 (27)</td>
<td>3H</td>
<td>1162 (10), 1133 (23)</td>
</tr>
<tr>
<td>2Br</td>
<td>1286 (4), 1256 (24)</td>
<td>3Br</td>
<td>1226 (6)</td>
</tr>
<tr>
<td>2NO3</td>
<td>1238 (20)</td>
<td>3NO3</td>
<td>875 (15)</td>
</tr>
</tbody>
</table>

*Measured at 25 °C on species labeled with 14N and 15N on the NO moiety. Full data are given in the Supporting Information. Syn ArN(O)N(O)Ar dimer. Contains a small amount of mononuclear species 3H. Anti ArN(O)N(O)Ar dimer.

IR Properties. In CDCl3, CD2Cl2, or acetone-d6 solutions, all 3R species display diamagnetic 1H and 13C NMR spectra (Figures S37–S47). For 3H, 3O, and 3Br, this indicates a singlet ground state, as was observed for similar η2 superoxocopper(II) species, this ground-state singlet is expected to be highly delocalized.64 This situation also contrasts with the end-on topology, where end-on superoxocopper(II) complexes have a S = 1 ground state, as do CuII(kO-ArNO−) complexes when Cu–O–N–CAr is coplanar.17

The 15N NMR spectra of the 15N-labeled 3R species are most informative on the degree of electron transfer (Figure 2).

Figure 2. 15N NMR data (50.7 MHz) of the 3R species (R = NMe3, H, Br, NO2), 15N-enriched at the NO position, in CDCl3 at 25 °C. Species 3H was made in situ by mixing equimolar amounts of TMPD, [Cu(MeCN)4](TfO), and 2R.

245 leads to a dramatic upshift of the signal by 550 ppm, consistent with the ArNO moiety being doubly reduced 248

Table 2. NO Stretching Frequencies

<table>
<thead>
<tr>
<th>species</th>
<th>ν (Δ)/cm⁻¹</th>
<th>species</th>
<th>ν (Δ)/cm⁻¹</th>
</tr>
</thead>
<tbody>
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<td>2NMe3</td>
<td>1365 (12), 1340 (19)</td>
<td>3NMe3</td>
<td>1392 (14), 1315 (6)</td>
</tr>
<tr>
<td>2H</td>
<td>1388 (27)</td>
<td>3H</td>
<td>1162 (10), 1133 (23)</td>
</tr>
<tr>
<td>2Br</td>
<td>1286 (4), 1256 (24)</td>
<td>3Br</td>
<td>1226 (6)</td>
</tr>
<tr>
<td>2NO3</td>
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<td>3NO3</td>
<td>875 (15)</td>
</tr>
</tbody>
</table>

*Measured at 25 °C on species labeled with 14N and 15N on the NO moiety. Full data are given in the Supporting Information. Syn ArN(O)N(O)Ar dimer. Contains a small amount of mononuclear species 3H. Anti ArN(O)N(O)Ar dimer.

with reduction of the bond order upon inner-sphere electron transfer from the Cu center(s). For mixed-valent dinuclear species 3H+, the NO stretch is lowered from 1385 to about 70–100 cm⁻¹, consistent with the electron density being delocalized onto the additional Cu(I) center.

NMR Properties. In CDCl3, CD2Cl2, or acetone-d6 solutions, all 3R species display diamagnetic 1H and 13C NMR spectra (Figures S37–S47). For 3H, 3O, and 3Br, this indicates a singlet ground state, as was observed for similar η2 superoxocopper(II) species, this ground-state singlet is expected to be highly delocalized.64 This situation also contrasts with the end-on topology, where end-on superoxocopper(II) complexes have a S = 1 ground state, as do CuII(kO-ArNO−) complexes when Cu–O–N–CAr is coplanar.17
The electronic structure of the complexes was probed by UV–vis absorption spectroscopy (Figure 3 and Table 3).

<table>
<thead>
<tr>
<th>species</th>
<th>$\delta^{(15)N}$/ppm</th>
<th>species</th>
<th>$\delta^{(15)N}$/ppm</th>
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</thead>
<tbody>
<tr>
<td>$^{3}$NMe$_2$</td>
<td>787.58</td>
<td>$^{3}$NMe$_2$</td>
<td>668.58</td>
</tr>
<tr>
<td>$^{3}$H</td>
<td>885.83</td>
<td>$^{3}$H</td>
<td>not observed</td>
</tr>
<tr>
<td>$^{3}$Br</td>
<td>878.67</td>
<td>$^{3}$Br</td>
<td>not observed</td>
</tr>
<tr>
<td>$^{2}$NO$_2$</td>
<td>913.23</td>
<td>$^{2}$NO$_2$</td>
<td>363.67</td>
</tr>
</tbody>
</table>

*Measured in CDCl$_3$ at 25 °C on a 500 MHz instrument; $\nu^{(15)N}$ = 50.7 MHz.

ArNO$_2$ and therefore quite electron-rich. Interestingly, no $^{15}$N signal was observed for $^{3}$H and $^{3}$Br under the same recording conditions or with a wider acquisition window. This behavior is consistent with the radical character of the ArNO$^+$ moiety in these species. A small amount of triplet character was made in the solid state. Overall, the NMR data confirm, in solution, the assignments that were made in the solid state.

**Ultraviolet–Visible (UV–Vis) Absorption Properties.** The electronic structure of the complexes was probed by UV–vis absorption spectroscopy (Figure 3 and Table 3).

![Figure 3. UV–vis spectra of $^{3}$R species in CH$_2$Cl$_2$ at 25 °C.](image)

<p>| Table 3. UV–Vis Data of $^{3}$R Complexes$^d$ |
|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>species</th>
<th>$\lambda_{max}$/nm $^b$</th>
<th>$\nu_{max}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{3}$NMe$_2$</td>
<td>426 (32.8)</td>
<td>358 (34.7)</td>
</tr>
<tr>
<td>$^{3}$H</td>
<td>318 (8.0), 538 (7.4)</td>
<td>440 (sh)</td>
</tr>
<tr>
<td>$^{3}$Cl</td>
<td>319 (10.2), 350 (7.3)</td>
<td>440 (sh)</td>
</tr>
<tr>
<td>$^{3}$Br</td>
<td>325 (10.4), 350 (8.2)</td>
<td>440 (sh)</td>
</tr>
<tr>
<td>$^{3}$NO$_2$</td>
<td>345 (19.4)</td>
<td>440 (sh)</td>
</tr>
</tbody>
</table>

$^d$Measured in CH$_2$Cl$_2$ at 25 °C. $^b$$\lambda_{max}$/nm ($\mu$/mM$^{-1}$ cm$^{-1}$).

Time-dependent DFT (TD-DFT) calculations were performed on the $^{3}$R complexes, and the predicted spectroscopic data provide calculated spectra that compare well with the experimental observations (Tables S4–S8 and Figures S15–S20). Our computations support that the UV–vis spectra of $^{3}$H, $^{3}$Cl, $^{3}$Br, and $^{3}$NO$_2$ are similar and dominated by two main absorption bands of different intensities, while that of $^{3}$NMe$_2$ displays two intense electronic transitions. For the latter, the band at 538 nm is assigned to a metal-to-ligand charge transfer (MLCT), and the band at 426 nm is attributed to a ligand-to-ligand charge transfer (LLCT). For both transitions, the acceptor states mainly involve the nitroso moiety (Figure S16). The electronic transitions for $^{3}$NO$_2$ were already analyzed. The 345 and 644 nm bands correspond to MLCT transitions involving the $\mu$-$\eta^2$-NO$^-$ moiety, in a very similar manner to the transitions in the ($\mu$-$\eta^2$-O$_2$-Cu$^2$)$_2$ cores that mimic the active sites of oxytrosinase and oxyhemocyanin. For $^{3}$H, $^{3}$Cl, $^{3}$Br, and $^{3}$NO$_2$, the absorptions near 320 nm are due to 2 MLCT and LLCT, with the acceptor state involving the NO moiety, while the transitions in the visible around 610 nm display a mixed character with similar contributions from the metal and the nitroso moiety in both donor and acceptor states (Figures S17–S19). Our TD-DFT calculations thus adequately reproduce the energy of the key features of the experimental spectra, which further support the geometries and electronic properties of the $^{3}$R complexes. Vibrational analysis also confirmed the experimental observations (vide supra).

Consequently, $^{3}$NMe$_2$ can be described as a Cu(I) complex, while $^{3}$H, $^{3}$Cl, and $^{3}$Br are CuI($^{3}$ArNO$^+$) species. The dimer $^{3}$H$^*$ is assigned to CuII–CuI($^{3}$ArNO$^+$) species, while $^{3}$NO$_2$ was previously shown to be a Cu(II)–Cu(II) complex with an ArNO$^2+$ moiety (2e-reduced ArNO).

**Electrochemical Studies.** Because this work aims at tuning the redox properties by simple substitution, we studied the electrochemical behavior of both precursors $^{2}$R and complexes $^{3}$R for the whole series of R substituents (NMe$_2$, H, Cl, Br, and NO$_2$). The goal was to correlate the electrochemical properties with the reactivity (0e, 1e, or 2e transfer) observed upon reaction with the [(TMPD)Cu I]$^+$ complex I and the H-atom-transfer (HAT) reactivity of the $^{3}$R complexes (see below). The data were also compared to existing records for analogous ArNO and O$_2$ complexes. Cyclic voltammetry (CV) studies were performed at a glassy-carbon working electrode in dry CH$_2$Cl$_2$ with 0.1 M NBu$_4$OTf as the supporting electrolyte. In what follows, all potentials are referenced to the Fe$^{3+}$/Fe$^{2+}$ couple. Significant differences were found for the Fe$^{3+}$/Fe$^{2+}$ couple.

Substituted Nitrosoarenes, $^{2}$R. CV studies of the free nitrosoarenes, $^{2}$R$^*$, led to the summary in Scheme 5. $^{2}$H$^*$ was first studied for a comparison with the literature. When scanned negatively, it displays two reversible responses at $E_{1/2}$.
An irreversible cathodic peak at $-1.17$ V was observed at faster scan rates.

### Table 4. Electrochemical Data of the 2\textsuperscript{R} Nitrosoarenes\textsuperscript{a}

<table>
<thead>
<tr>
<th>species</th>
<th>$E_{1/2}^{1/2}(2\text{R})$</th>
<th>$E_{pc}^{1/2}(2\text{R})$</th>
<th>$\sigma_{para}$\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\text{NO}_2$</td>
<td>$-1.40$ (100)</td>
<td>$-1.86$ (100)</td>
<td>$0$</td>
</tr>
<tr>
<td>$3\text{Cl}$</td>
<td>$-1.32$ (110)</td>
<td>$-1.79$ (90)</td>
<td>$0.227$</td>
</tr>
<tr>
<td>$3\text{Br}$</td>
<td>$-1.30$ (90)</td>
<td>$-1.75$ (90)</td>
<td>$0.232$</td>
</tr>
<tr>
<td>$3\text{H}$</td>
<td>$-0.91$ (90)</td>
<td>$-1.33$ (100)$^c$</td>
<td>$0.78$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In CH$_2$Cl$_2$ containing 0.1 M NBu$_4$OTf at 25 °C (glassy-carbon working electrode); scan rate $\nu = 0.1$ V s$^{-1}$, E/V versus Fc$^{+/0}$ ($\Delta E_p$/mV). \textsuperscript{b}$\sigma_{para}$ Hammett parameters. \textsuperscript{c}Determined at $\nu = 0.5$ V s$^{-1}$. \textsuperscript{d}Not determined. \textsuperscript{e}An intermediate wave at $-1.17$ V was observed at faster scan rates.

### Table 5. Electrochemical Data of 3\textsuperscript{R} Complexes\textsuperscript{a}

<table>
<thead>
<tr>
<th>species</th>
<th>$E_{1/2}^{1/2}(3\text{R})$</th>
<th>$E_{pc}^{1/2}(3\text{R})$</th>
<th>$E_{1/2}^{1/2}(3\text{R})$</th>
<th>$\sigma_{para}$\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3\text{NO}_2$</td>
<td>$-1.05$</td>
<td>$-0.92$</td>
<td>$-1.45$</td>
<td>$0.28$</td>
</tr>
<tr>
<td>$3\text{Cl}$</td>
<td>$-0.82$</td>
<td>$-1.22$</td>
<td>$0.08$</td>
<td>$0.23$</td>
</tr>
<tr>
<td>$3\text{Br}$</td>
<td>$-0.72$</td>
<td>$-1.17$</td>
<td>$0.11$</td>
<td>$0.78$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In CH$_2$Cl$_2$ containing 0.1 M NBu$_4$OTf at 25 °C; scan rate $\nu = 0.1$ V s$^{-1}$, E/V versus Fc$^{+/0}$ ($\Delta E_p$/mV). \textsuperscript{b}$\sigma_{para}$ Hammett parameters. \textsuperscript{c}Irreversible cathodic peak.
The reaction is written in a way it was carried out either as an oxidation or as a reduction. Abbreviations: n/c, compound not characterized; P, cis-end-on peroxo; S, cis-end-on peroxo; P, side-on peroxo; O, bis(μ-oxo). Reversible versus Fc. "Irreversible cathodic peak. "Reversible reduction. "Reversible oxidation. Converted from the value versus saturated calomel electrode (SCE) using E_{1/2}(Fc|FcO) = 560 mV versus SCE in these conditions.

Scheme 6. Thermodynamic Analysis of HAT Reactivity

\[
\begin{align*}
\text{Cu}_2(\text{ArNO})^\text{2−} & \quad \text{BDE(N-H)} & \quad \text{Cu}_2(\text{ArN(H)}O)^\text{2−} \\
3\text{R} & \quad E^C & \quad 3\text{H} \\
& \quad pK_a(N-H) & \quad \text{BDFE(DHA-H)} = 1.47pK_a + 23.06E^C + C \quad (\text{Eqn. 1})
\end{align*}
\]

Table 6. Electrochemical Data of 3R and Related Ni_{n/2}/ArNO and Cu_{n/2}/O_2 Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>(E^i)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n/c</td>
<td>-0.92</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>n/c</td>
<td>-0.89</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>n/c</td>
<td>-1.53</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>n/c</td>
<td>-0.59</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>n/c</td>
<td>-0.36</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>n/c</td>
<td>-0.01</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>n/c</td>
<td>-0.75</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>n/c</td>
<td>-0.72</td>
<td>This work</td>
</tr>
</tbody>
</table>
distilled over CaH2 under nitrogen and stored in the glovebox. The copper salt [(MeCN)4Cu](TfO) was prepared by adapting the Kubas procedure using TfOH. 4-3
Dimethylaminonitrosobenzene (2NMe) and 4-chloronitrosobenzene (2Cl) were prepared via literature procedures. Isotopically labeled 15N-4-nitrosonitrosobenzene and [(TMPPCu)(µ-T)O(µ-η2-η1-p-NO2-C6H4(NO)](TfO) were prepared following the procedure reported earlier. 4-Bromoamine-15N was prepared from 15N-acetamide as reported in the Supporting Information. 15N derivatives of 2H, 2D, and 2D were prepared similarly to the 15N samples (see the Supporting Information).

**Characterization Methods.** NMR spectra were recorded on a Varian Inova-500 MHz instrument. All spectra were recorded in CDCl3, unless otherwise noted. 1H and 13C NMR spectra were referenced to internal tetramethylsilane. For 13C, the signal for the TFO- anion is not reported; it is observed at 119.5 ppm in concentrated samples. 15N NMR spectra were referenced to external formamide in dimethyl sulfoxide. IR spectra were recorded on a Nicolet iSS (Thermo Scientific) attenuated-total-reflectance instrument. UV–vis spectra were recorded on an Agilent 8453 spectrophotometer or a B&W Tek i-Trometer. Elemental analysis was performed by the Laboratoire d’Analyse Élémentaire de l’Université de Montréal. The presence of F atoms in the samples interfered with the normal integration peak for H atoms. The value for H is not necessarily trustworthy.

**X-ray Crystallography.** Crystallographic analysis was performed on a Bruker APEX-DEU diffractometer. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multiscan method (SADABS or TWINABS). The structures were solved by direct methods and refined using the APEX3 software package. All non-H atoms were refined with anisotropic thermal parameters. H atoms were generated in idealized positions, riding on the carrier atoms with isotropic thermal parameters.

**Electrochemistry.** Room temperature electrochemical studies of the nitrosoarene ligands and their copper complexes were performed in a glovebox (Jacomex; O2 < 1 ppm and H2O < 1 ppm) with a homemade three-electrode cell (WE, glassy carbon or platinum; RE, platinum wire in a FC/Fc solution; CE, platinum or graphite rod). Ferrocene was added at the end of the experiments to determine the redox potential values. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 Metrehot) potentiostat monitored by the NOVA 111 software. Dichloromethane (Acros) was distilled over CaH2 under an inert atmosphere and stored in a glovebox. The supporting salt NBUHFE was synthesized from NBUH(OAc) and HFPr (Aldrich). It was then purified, dried under vacuum for 48 h at 100 °C, and then kept under argon in the glovebox. NBUHDT (Aldrich, 99%) was stored as received in the glovebox. Electrolytic solutions were prepared in the glovebox and dried for a few days under molecular sieves (3 A) to remove traces of water before use.

**Computational Details.** All theoretical calculations were performed with the ORCA program package. Full geometry optimizations were carried out for all complexes using the generalized gradient approximation functional (B) in combination with the TZV/ basis set for all atoms and by taking advantage of the resolution of the identity (RI) approximation in the Split-RI variant with the appropriate Coulomb fitting sets. Increased integration grids (Grid4 in the ORCA convention) and tight self-consistent-field convergence criteria were used. IR spectra were obtained from numerical frequency calculations performed on DFT-optimized structures. Isotope shift effects (15N/15N) were taken into account using the orca subutility program, and vibrational normal modes were visualized with Chemcraft software. Solvent effects were accounted for according to the experimental conditions. For that purpose, we used the CH2Cl2 (ε = 9.08) solvent within the framework of the conductor-like screening (COSMO) dielectric continuum approach. Single-point optical properties were predicted from additional single-point calculations using the same functional/basis set as that employed previously. Electronic transition energies and dipole moments for all models were calculated using TD-DFT (101–103) within 600 hartree.
Experimental supplements, including a crystallography table, a Job plot, $^{15}$N labeling, IR data, electrochemistry supplements, DFT data, and NMR spectra (PDF).

Accession Codes
CCDC 1959040–1959043 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions
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Notes
The authors declare no competing financial interest.

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Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.inorgchem.9b03175.


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